A New Method for the Gravimetric Determination of Zirconium

(Hafnium not differentiated)

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

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WILLIAM J. YOUDEN, JR., B.S., M.A.
NEW YORK CITY
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INTRODUCTION

The extreme insolubility of the precipitate resulting from the addition of orthophosphate ion to a solution of a zirconium salt has led many investigators to use it as a basis for the estimation of this element. The number of insoluble phosphates is large but very few of them are as insoluble as zirconium phosphate. The solubility product for this salt is exceeded even in the presence of six normal sulphuric acid. It is this feature that was counted on to permit the separation of zirconium from other elements. The precipitate is, however, extraordinarily bulky and tends to carry down iron with it. A more serious defect is the failure of the ignited precipitate to correspond to any simple formula. These and other criticisms to be brought out later made it seem desirable to undertake further work on the quantitative determination of zirconium.

The fact that the arsenates show some parallelism with the phosphates as to solubility, being usually more soluble led to the conclusion that zirconium arsenate might be sufficiently insoluble for quantitative use. Insoluble zirconium arsenates have been reported by Paykull [1] and Kulka [2]. The former made no analytical application of this compound. The work of the latter is not available but it may be safely assumed that no method for the determination of zirconium was based upon its use since the literature of analytical chemistry contains no reference to it. The arsenate has the disadvantage that strongly acid solutions might depress the concentration of arsenate ions to a very low value and so prevent precipitation of the zirconium arsenate since arsenic acid is a weaker acid than phosphoric. Provided, tho, that zirconium arsenate is sufficiently insoluble, there is gained the important advantage of the increased solubility of the arsenates over the

(1) Bull. Soc. chim. 20, 65, (1873)
(2) Dissertation. Bern 1902.

corresponding phosphates of the other elements that might be present. Preliminary work showed that the addition of an arsenic acid solution to a zirconium solution precipitated the zirconium so completely that no further precipitate was obtained on adding phosphate ion. It was established that the zirconium arsenate was quantitatively thrown down by arsenate ion in the presence of sulphuric acid having a maximum concentration of approximately three quarters normal. It was also observed that the zirconium arsenate was more dense than the phosphate precipitate, a very desirable condition.

It was found on ignition that the zirconium arsenate precipitate yielded the oxide of zirconium, which may or may not be contaminated with hafnium.

Hevesy and Valdemer [3] using the method of x-ray analysis have shown that many zirconium ores contain the newly discovered element hafnium. Usually the hafnium content is under 3 percent, tho in one case they found about 30 percent of hafnium. The chemical properties of hafnium [4] are closely related to those of zirconium. Hevesy and Jantzen [5] have separated hafnium from zirconium by fractional crystallizations of the ammonium flourides. Evidently the chemical status of hafnium is not sufficiently well established to permit of its separate consideration in analytical work on zirconium materials. Hence in this work reference to "pure" zirconium compounds means freedom from the well established elements usually associated with zirconium and does not differentiate hafnium.

The conversion of the arsenate to the oxide by ignition is a point of extreme importance because the composition of the ignited phosphate precipitate is a matter of controversy. Further, in establishing the accuracy of the arsenate method both as to completeness of precipitation and as to separation of zirconium from other elements with which it is commonly associated, it allows a direct com-

(3) J. Chem. Soc. 123, 3218 (1923)
(4) Hevesy, Chem. News 127, 186 (1923)
(5) Chem. News 127, 353 (1923)

Their procedure was followed in making analyses by the parison of the results obtained by the arsenate method with those obtained by precipitating zirconium hydroxide from a standard solution of a pure zirconium salt with ammonium hydroxide and subsequent ignition to the oxide. The fact that the same product is obtained by precipitating the arsenate and igniting and by precipitating the hydroxide and igniting is significant because no calculations using the doubtful atomic weight of zirconium are necessary.

THE PHOSPHATE METHOD

In the course of this work data pertinent to the question of the composition of the ignited phosphate precipitate have been collected. The recent paper by Lundell and Knowles [6] also bears on this point. They specify the following conditions for the precipitation of zirconium phosphate:

Volume of solution.—From 25 c.c. for small amounts (0.005 g. ZrO_2) to 200 c.c. for larger amounts (0.1 g. ZrO_2).

Acidity.—20% sulphuric acid by weight.

Hydrogen peroxide.—Sufficient to keep the titanium dioxide peroxidized. 10 c.c. do no harm.

Precipitant.—Secondary ammonium phosphate in excess. From 10 to 100 times the theoretical requirement as expressed by the ratio Zr : P_2O_5 should be used. The larger excess is desirable when small amounts of zirconium are to be determined.

Precipitating conditions.—(1) Temperature: Cold or 40 to 50°C. Preferably the latter. (2) Time: Two hours for amounts of ZrO_2 in excess of 0.005 g.: six hours or longer for smaller amounts.

Filtration:—Warm, decant as much supernatant liquid as possible to avoid clogging the filter.

Washing.—With cold 5% ammonium nitrate solution.

Ignition.—Very careful ignition in a partially covered platinum crucible over a low flame until the filter paper carbon is destroyed, followed by blasting or its equivalent.

(6) J. Am. Chem. Soc. 41, 1801 (1919)

phosphate method except that in washing the precipitate a hot solution containing 5% nitric acid and 5% ammonium nitrate was used. The purpose of the acid was to prevent hydrolysis of the zirconium salt to any basic modification.

Lundell and Knowles claim to have shown that the ignited phosphate precipitate may be assigned the formula ZrP_2O_7. The ratio of oxide to phosphate for this salt is 0.4632 taking the atomic weight of zirconium as 90.6. The experimental ratio obtained by these workers in a series of analyses made under the conditions finally adopted was 0.4713. This value is in substantial agreement with the experimental factor, 0.4733, obtained in our work altho quantities much larger than they employed were used. The evidence does not warrant the conclusion that the residue is zirconium pyrophosphate.

Assuming that hafnium were present it would probably be included in any analysis made due to its reported chemical similarity to zirconium. In this case it is obvious that there is no possible way of calculating the combined oxides from the weight of phosphate precipitate.

Part of the confusion in the matter of the formula of the ignited phosphate precipitate may be traced to the uncertainity in the atomic weight of zirconium. The value listed in the last atomic weight table is 90.6. This estimate dates since 1899. It is based on determinations which vary almost three units among themselves and all but one of which were made before 1890. Venable [7] published a determination in 1898 giving the value 90.81. More recently Venable and Bell [8] obtained the value 91.76 for the atomic weight of zirconium. On this basis the theoretical factor for the ratio of oxide to pyrophosphate becomes 0.4654. There is little profit in comparing the experimental and calculated factors until the atomic weight of zirconium is more accurately established.

OTHER METHODS

A very good discussion of the analytical chemistry of zirconium, including a list of methods of historical interest, is

(7) J. Am. Chem. Soc. 20, 118 (1898)
(8) J. Am. Chem. Soc. 39, 1598 (1917)

given in Bulletin 212, Department of the Interior, "Analytical Methods for Certain Metals". Two other compilations which are valuable especially for the very complete bibliographies included are Bulletin 186, Department of the Interior, "Investigations of Zirconium with Especial Reference to the Metal and Oxide" and the American Chemical Society Monograph "Zirconium" by Venable.

Several methods involving the use of faintly acid solutions of zirconium salts have been proposed. A wide variety of reagents are listed all having the common purpose of lowering the hydrogen ion concentration. Either zirconium hydroxide or a very basic salt of zirconium is precipitated on addition of the reagent. The well known tendency of zirconium salts to undergo hydrolysis makes it very difficult to obtain the required low concentration of hydrogen ion without precipitating the zirconium before the reagent is added. Again the procedure is very unfavorable for separations since it is most difficult to adjust the conditions so finely that only the zirconium will precipitate.

Many organic substances will precipitate zirconium. Some of these are merely sources of hydroxyl ion. Others, which are employed in acid solution, give insoluble products with many other elements, so that tedious preliminary separations are required.

A method employing a 5% hydrochloric acid solution was advanced by Smith and James [9] in which a solution of selenious acid was used as the precipitant.

The precipitate on ignition is converted to the oxide. The method is limited to hydrochloric acid solutions free from sulphate ion. According to the authors iron interferes when present in quantities in excess of 10% of the zirconium. The almost universal association of zirconium with iron limits this method to relatively few cases.

(9) J. Am. Chem. Soc. 42, 1765 (1920)

THE ARSENATE METHOD

The preliminary experiments in this investigation having shown that zirconium arsenate possessed many characteristics which made it suitable for the gravimetric determination of zirconium, a number of analyses were made with the view to establishing a definite procedure. The following method was developed: Adjust the solution containing zirconium to an acidity not greater than 0. 1 N with respect to either hydrochloric or sulphuric acid and to a volume of approximately 250 c.c. Add 5-10 c.c. of hydrogen peroxide in case titanium or ceric ions are present, 15 c.c. of 6 N sulphuric acid, and heat until the temperature is above 60°C. The reagent, in amount equal to ten times the theoretical (assuming normal zirconium arsenate), is added slowly with stirring. After standing two hours or longer decant the liquid and wash at least twice by decantation using about 200 c.c. of hot water each time. The nature of the precipitate is improved by heating and stirring for 2 or 3 minutes after adding the hot water. Wash the precipitate on to the filter paper and complete the washing with hot water. Transfer the filter to a weighed silica crucible and heat over a Bunsen burner for a short time. The ignition is completed over a Meeker burner taking care to obtain the maximum temperature. Asbestos cylinders about four inches in diameter with slots to support the triangle greatly increase the efficiency of ignition. Most of the arsenic usually volatilizes in an hour and two or three subsequent heatings suffice to bring the contents of the crucible to constant weight.

Modification of the Method in the Presence of Iron

The procedure outlined above was found satisfactory in the absence of iron. While iron yields no precipitate under the conditions established the zirconium oxide is discolored by iron which is carried down by adsorption. The error due to this effect was avoided by substitution of the following procedure: The solution is prepared for analysis as given above, but before adding the arsenate reagent several grams

of ammonium thiocyanate are introduced. On addition of the arsenic acid the zirconium arsenate precipitates and the iron remains in solution as molecular ferric thiocyanate. The decantations are performed by adding 3-4 grams of thiocyanate salt, 50 or more c.c. of 0.3 N sulphuric acid, a few c.c. of arsenate reagent, and hot water. This procedure is very satisfactory in the presence of moderate quantities of iron. In the presence of large amounts of iron it is necessary to carry out a double precipitation. In this event the precipitate is washed twice by decantation as just described. Then add to the residue in the beaker 15 c.c. of 6 N sulphuric acid and swirl until the precipitate dissolves. It may be warmed gently if required. Several grams of ammonium thiocyanate are then added, the solution diluted to 250-300 c.c. and arsenate reagent added. After a couple of hours the solution is decanted and the residue washed twice by decantation (using thiocyanate).

DISCUSSION

Freshly precipitated zirconium arsenate somewhat resembles silver chloride in appearance. It has about half the bulk of the phosphate precipitate, settles rapidly, and permits sharp decantations. The gelatinous nature of the phosphate precipitate requires washing by decantation which in this case is an exceedingly inefficient operation. The difference between the arsenate and phosphate precipitates is so marked that the time required for washing is cut in half by the arsenate method. On ignition the arsenate precipitate yields zirconium oxide which is extremely infusible, nonhygroscopic, and definite in composition, whereas the phosphate method requires an empirical factor.

The usefulness of any method depends largely on the effectiveness of the separation of the element from other elements commonly present. It was from the viewpoint of meeting this requirement that the arsenate method seemed so promising. Analyses were made in the presence of iron, aluminum, chromium, titanium, vanadium, and cerium, these

being the elements most often encountered in the analytical chemistry of zirconium. The results proved that none of these elements interfere except iron. The arsenates of titanium and cerium (in the ceric state) are insoluble but are prevented from precipitating by adding hydrogen peroxide. Iron is not precipitated by arsenate ion under the conditions given and the contamination of the zirconium arsenate precipitate by iron must be due to adsorption. To meet this situation a method had to be devised to tie up the iron as a soluble complex or molecular compound. The conversion of ferric iron to ferrous by the addition of sulphur dioxide failed to prevent adsorption. Fluoride ion which forms a complex ion with iron also forms a very stable one with zirconium, and decreases the concentration of zirconium so far that no precipitate is obtained on adding either arsenate or phosphate ions. On the other hand. thiocyanate ion forms a soluble molecular compound with iron but does not interfere with the precipitation of the zirconium as the arsenate. It may be that there are other ways of securing the same result.

Other elements which are not precipitated by arsenate ion under the conditions governing the analysis are thorium, nickle, cobalt, zinc, copper, manganese, uranium, tungsten, and thallium.

Attempts were made to establish the composition of the arsenate precipitate. A quantity of the precipitate was washed twice by decantation, 200 cc.c. of water added and then frozen [10]. When the ice melted the precipitate had decreased greatly in bulk and appeared fine and granular. It was washed into a weighed Gooch crucible and dried in 110°C. The product is difficult to weigh for it takes on weight in the air. When it no longer lost weighf on further drying it was ignited to constant weight. The loss was taken to be arsenic oxide and water and the residue zirconium oxide.

(10) Oakes, Dissertation, Columbia University, (1924).

Wt. Dried arsenate	Wt. ignited arsenate	Ratio
.1218	.0516	0.4236
.1377	.0577	0.4190

While the two analyses are not in perfect agreement they serve as a partial test of any proposed formula. Thus for $Zr_3(AsO_4)_4 \cdot 2H_2O$ the calculated ratio is 0.4258 which is not far from the values obtained.

PREPARATION OF SAMPLES FOR ANALYSIS

Two lots of zirconium oxychloride were obtained. One, from the Lindsay Light Co., was labeled 97-98% pure; the other obtained from the Welsbach Co., was supposed to be "C.P.". Judging from the color of the first mother liquor the "C.P." salt contained more impurities than the commercial variety. Purification of both salts was effected by repeated recrystallizations from concentrated hydrocholoric acid. For the first two or three crystallizations the hot solutions were poured thru an asbestos pad in a hot water funnel. After cooling the crystals were sucked as free as possible from the mother liquor. A small perforated gold cone at the apex of a glass funnel was used to support the salt. The final products after ten recrystallizations gave negative tests for iron and titanium. The ratio of oxide to phosphate for the purified products was found to be 0.4719 and 0.4746. These values taken in conjunction with the value 0.4713 obtained by Lundell and Knowles [11] afford strong evidence of the purity of the materials; for it is unlikely that impurities not removed by crystallization from hydrochloric acid would be present in all three materials to the same extent.

A part of the purified oxychloride was evaporated with sulphuric acid. The salt which separated on cooling was used to prepare solutions of zirconium sulphate. Solutions of the oxychloride were prepared in 0.3 N hydrochloric acid and of the sulphate in 0.3 N sulphuric acid. This prevented basic salts from separating from the solutions. All analyses were made on solutions so prepared.

(11) loc. cit.

REAGENTS

The reagent used for precipitating zirconium arsenate contained 7.5 grams of arsenic oxide per 100 c.c. of solution. At first a water solution of C.P. arsenic oxide was used. Examination of the arsenic oxide showed that it contained a large amount of nonvolatile matter. A reagent free from nonvolatile matter was obtained by oxidizing some sublimed arsenious oxide either with chlorine or nitric acid. In the one case the excess of nitric acid was removed by evaporation with sulphuric acid. In the other the solution was freed from chlorine by boiling.

Table I

Data showing constant composition of ignited phosphate p'pt. Zirconium oxychloride (Lindsay) recrystallized 3 times. Solution A. 50 c.c. portions.

	c.c. conc. H_2SO_4 in 200 c.c. of solution			
Reagent—grams	23	35	6	11
1.5				
	.2199	.2207	.2190	.2206
	.2202	.2187	.2201	
	.2196	.2205	.2188	
	.2206	.2206	.2197	
	.2201			
	.2200			
3.0	.2210			
	.2201			
0.75	.2201			

Table II

Zirconium oxychloride (Lindsay) recrystallized 6 times. Solution B. 50 c.c. potions.

	Phosphate precipitate	Oxide by ammonia
	.1643	.0776
	.1651	.0771
	.1647	.0774
Average	.1647	.07737

Factor 0.4698

Table III

Zirconium sulphate (Lindsay) recrystallized 6 times. Solution C. 50 c.c. portions.

	Phosphate precipitate	Oxide by ammonia	Oxide by arsenate	Remarks on arsenate method c.c 6N H_2SO_4	Other elements present
	.1223	.0572	.0572	12	
	.1222	.0574	.0574	12	Ti 5 mg.
	.1218	.0573	.0571	12	Ce
			.0572	10	
Ave.	.1221	.0573	.0578	15	
			.0578	15	
	Factor	0.4693	.0566	15	Fe 20 mg.
			.0582	15	Fe 20 mg.
			.0564	10	
			.0579	15	Fe 20 mg.
		Ave.	.05736		

Table IV

Zirconium oxychloride (Lindsay) recrystallized 10 times.

Solution D. 50 c.c. portions.

Phosphate precipitate	Oxide by ammonia	Oxide by arsenate	Remarks on arsenate method: c.c. 6N H_2SO_4	Other elements Present
.1967	.0927	.0924	30	
.1967	.0930	.0926	30	
.1966	.0931	.0924	30	
.1971	.0930	.0928	30	
		.0926	24	
Ave. .19678	.09295	.0929	24	
		.0924	24	Ti 10 mg.
Factor 0.4724		.0922	24	Ti 5 mg.
		.0929	18	
		.0930	18	
		.0926	18	
		.0928	12	
		.0928	6	
		.0933	0	
		.0933	15	Al 10 mg.
	Ave.	.09273		

TABLE V

Zirconium oxychloride (Lindsay) recrystallized 10 times.

Solution E. 50 c.c. portions.

Phosphate precipitate	Oxide by ammonia	Oxide by arsenate	c.c. 6N H_2SO_4	Remarks on arsenate method Other elements present
.2233	.1054	.1054	24	
.2236	.1053	.1055	24	
	.1052	.1054	24	
	.1054	.1057	24	
		.1062	24	
Ave. .22345	.10533	.1060	15	
		.1047	15	
Factor 0.4714		.1051	12	
		.1062	12	
		.1055	10	
		.1051	10	
		.1060	10	
		Ave. .10557		

TABLE VI

Zirconium oxychloride (Welsbach) recrystallized 10 times.

Solution F. 50 c.c. portions.

Phosphate precipitate	Oxide by ammonia	Oxide by arsenate	c.c. 6N H_2SO_4	Remarks on arsenate method Other elements present
.1169	.0556	.0558	15	
.1175	.0553	.0548	15	Vanadium
.1173	.0552	.0550	15	
.1169	.0558	.0549	12	
	.0561	.0559	10	
		.0560	10	
Ave. .11715	.0556	.0559	10	
		.0555	6	
Factor 0.4746				
		Ave. .0555		

Table VII

Zirconium oxychloride (Welsbach) recrystallized 10 times.

Solution G. 25 c.c. portions.

Phosphate precipitate	Oxide by ammonia	Oxide by arsenate	c.c. N6 H_2SO_4	Remarks on arsenate method Other elements present
.1302	.0619	.0623	15	
.1304	.0617	.0614	15	
	.0618	.0616	15	
	.0620	.0620	15	
Ave. 1303	.06185	.0619	15	Chromium 20 mg.
		.0624	15	
	Ave. .06195			
Factor 0.4747				
		.0620	10	
		.0622	10	
		.0617	10	
		.0623	10	
		Ave. .06205		

EXAMINATION OF DATA

Each table represents analyses conducted on a particular solution of pure zirconium salt. The zirconium oxide content of each solution was determined by pipetting a portion, adding ammonium hydroxide, and igniting the precipitated hydroxide to the oxide. The average of four analyses was taken for the purpose of comparing with the arsenate method. The average weight of oxide by the arsenate method agrees with the average weight of oxide by ammonia within three parts per thousand. This is a very searching comparision because the conditions for the arsenate method vary greatly within each table. Thus in Table IV the acidity ranges from almost normal to less than one tenth normal in sulphuric acid. In Table VII the average of seven analyses made under the recommended conditions differs by one part in six hundred from the average obtained by the reference

method. The average deviation for these seven analyses from the average (0.06195) is 0.26 milligram. No discrepancies appear in the weight of zirconium oxide in those analyses made in the presence of other elements.

SUMMARY

A survey of the analytical methods for zirconium has been made including an experimental study of the phosphate method.

A new method for the gravimetric determination of zirconium has been outlined which possesses the following advantages:

(a) The method is applicable over a wide range of acidity. The analyses are not affected by changes in acidity from one tenth to three fourths normal in sulphuric acid.

(b) The substance weighed is zirconium dioxide which is definite in composition, stable toward heat, and non-hygroscopic.

(c) Hot water is used for washing the precipitate thus obviating the necessity of special wash solutions.

(d) Because of the flocculent character of the precipitate the filtration is much more rapid than is the case with the gelatinous phosphate precipitate.

(e) The reagent employed is a solution of arsenic acid which is readily obtained in a pure condition.

(f) The method gives accurate separations of zirconium from a very large number of elements and especially such elements as iron, aluminum, chromium, titanium, cerium, and vanadium some or all of which are present in zirconium analyses.

VITA

William J. Youden, Jr., was born in Townsville, Australia, April 12, 1900. He received the degree of B.S. in Ch. E. from the University of Rochester in June 1921; and was then appointed Instructor in Chemistry in the same institution, a position which he held for one year. In September, 1922, he began graduate work as University of Rochester Scholar in the Schools of Mines, Engineering and Chemistry in Columbia University. Since February 1923 he has been a graduate student in the Department of Chemistry, Columbia University, receiving the degree of M.A. in June, 1923. During the year 1923-1924 he held an appointment as Assistant in Chemistry.